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# “Nature and Estimated Human Toxicity of Polar Metabolite Mixtures in Groundwater Quantified as TPHd/DRO at Biodegrading Fuel Release Sites,”

Article in *Ground Water Monitoring and Remediation* · April 2014

DOI: 10.1111/gwmr.12053

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## Discussion of Paper

"Nature and Estimated Human Toxicity of Polar Metabolite Mixtures in Groundwater Quantified as TPHd/DRO at Biodegrading Fuel Release Sites," by D.A. Zemo, K.T. O'Reilly, R.E. Mohler, A.K. Tiwary, R.I. Magaw, and K.A. Synowiec, 2013, v. 33, no. 4: 44–56.

**Comment** by Roger C. Brewer<sup>1</sup> and Uta Hellmann-Blumberg<sup>2</sup>

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The discussions of the chemistry and toxicity of total petroleum hydrocarbon (TPH) breakdown products in water in a recent article by Zemo et al. (2013) and in a companion paper by the same authors (Mohler et al. 2013) are welcome and much needed. Biodegradation of the parent hydrocarbon mixture typically produces a variable and changing mix of alcohols, phenols, aldehydes, and ketones and acids/esters as they ultimately break down to carbon dioxide and water. A better understanding of the risks posed to drinking water resources, humans, and aquatic habitats by these polar breakdown products will help reduce uncertainty regarding the need for additional actions at petroleum-contaminated sites.

However, Zemo et al. unfortunately stop short of providing a clear pathway forward to resolve this issue, and at this time it is still necessary to assess the environmental risk posed by petroleum-related, breakdown compounds in conjunction with the parent compounds. Polar compounds can indeed be removed from a sample by passing the extract through a column or cartridge packed with silica adsorbent, a process referred to as "silica gel cleanup" or "SGC," as they describe (US EPA 1996). Naturally occurring polar compounds might also be present in groundwater samples. The proportion of these compounds is generally minimal in comparison to petroleum-related polar compounds at contaminated sites, however, and the former cannot be selectively identified and/or removed from the sample using SGC. The authors imply that SGC should be routinely used for all groundwater samples if data are to be compared to

risk-based screening levels for TPH or used in quantitative risk assessments (e.g., MADEP 2002; HDOH 2011; CalEPA 2013a). Doing so, however, is only technically defensible if a quantitative method is available to separately assess the human health and ecological risk posed by the polar compounds. This is important, since the toxicity of a compound is often mediated by its intermediate metabolites. Of particular interest are the metabolites of surrogate compounds used to derive toxicity factors for TPH aliphatic and aromatic carbon ranges (Edwards et al. 1997; USDHHS 1999; MADEP 2003; WDOE 2006; US EPA 2009; CalEPA 2013b).

Zemo acknowledges that "This study did not develop 'screening levels' for the polar metabolites in groundwater for site management purposes (which would be a significantly more complex effort than appropriate for this study)." They instead present a semi-quantitative ranking of metabolite structural classes as "Low," "Low to Moderate," and "Moderate" based on a literature review of the toxicity of a limited number of individual compounds within each class of polar compounds. While omitting comparisons to parent hydrocarbons they conclude "These results (i.e., data for five sites referenced in the paper) indicate that the mixtures of polar metabolites identified in groundwater extracts at these five sites are unlikely to present a significant human health risk, assuming that the affected groundwater were to be consumed as drinking water." Drawing such a conclusion is premature, however, since risk is assessed in quantitative terms of both toxicity and *exposure*. While it is good news that the majority of the TPH-related metabolite compounds they were able to identify belong to classes that are typically of "low" toxicity, such compounds could still pose significant health risk at high enough exposures.

This has important implications, since the ultimate recommendation of the paper seems to be that water samples be routinely processed using SGC for final decision-making purposes. This is not technically defensible at this time for multiple reasons, including:

- The TPH-related, polar compounds removed can represent the dominant proportion of organic chemicals in the water.
- The risk posed to human health by these contaminants in terms of toxicity and potential exposure cannot, at this time, be separately assessed and quantified with respect to the parent, nonpolar compounds.
- Taste and odor thresholds often drive the need for further action when drinking water resources are impacted by "low-toxicity" contaminants (e.g., refer to drinking water screening levels presented in HDOH 2011 and CalEPA 2013a).

- Toxicity to benthic and aquatic organisms must also be considered in cases where there is a potential for discharge of contaminated groundwater into streams, rivers, wetlands, coastal shoreline areas, or other aquatic habitats.

Excluding petroleum-derived polar compounds will underestimate potential impacts to groundwater and surface water quality from petroleum-related contamination (see also Lang et al. 2009). Given uncertainties regarding TPH-related breakdown products in groundwater and surface water, it is reasonable to include the concentration of polar breakdown products under the umbrella of “TPH” and delay the routine use of SGC until such time that quantitative methodologies to assess the risk posed by these compounds can be developed. In the interim, SGC can be a very useful tool for assessment of the nature and extent of natural attenuation at a petroleum-release site. As appropriate, this information can then be used to support a case for long-term management of residual contamination (+/- continued monitoring), over additional and in many cases costly and ineffective active remediation.

## Acknowledgments

The authors wish to thank colleagues who provided input on SGC and earlier drafts of this letter.

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